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NOTE ON EVAPORATION IN POROUS MEDIA

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ABSTRACT. Factors are discussed which govern evaporation of liquid in the small capillaries of a porous medium. Attention is directed to sheet-like aggregates from which the vapor can escape with little obstruction. Marked temperature gradients are then found to be confined to close neighborhoods of the menisci and evaporation is shown tc proceed in statiscally quite unstable configurations under a dynamic balance of surface tension, local evaporation rate and viscous shear. Estimates of evaporation rates and fluid velocities are given. The results discourage constitutive theories for porous media because mere size of capillaries, independently of shape and chemistry, is found to change the physical processes underlying macroscopic behavior.

I. INTRODUCTION. The following study was prompted by recognition that little is known about the physics of evaporation in fabrics beyond the guess that the rate of heat supply may equal the rate of latent-heat expenditure. Fabrics come in a great variety of very different structures and as a first step, a structure characteristic of "typical" porous media is here envisaged in which the solid matrix is threaded by an irregular network of interconnecting, small capillaries along each of which the capillary bore varies greatly over relatively small distances. The immediate challenge is then to isolate some of the many interacting, physical processes in a single capillary in order to distinguish those which really govern evaporation there; macroscopic descriptions must needs reflect the insights thereby gained.

A key restriction that helps in dividing the difficulties is to focus attention on sheet-like media which are thin in one direction, like fabrics, because the escape of the vapor is then relatively unobstructed and consideration of the processes in the vapor can be postponed (to Section VIII). At first sight, evaporation might be expected to be controlled by the manner of heat supply, but for capillaries of realistically small size, most forms of heat supply have similar effects because heat transfer across the capillary wall is then always important. Since the physical signposts diverge, unless one be quite specific, attention is restricted to liquids similar to water, to pressures and temperatures typical of the outdoors, and to throat diameters of about 10^{-4} to 10^{-2} cm. A final dividing step is to start with an unrealistic configuration of geometrical and thermal symmetry in which only a single meniscus needs to be considered (Section III, IV).

Analysis of the simple thermal balances for that case shows that significant temperature gradients can occur only very close to menisci (Section IV), and a rough estimate of evaporation emerges (Section IV).

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It shows the symmetrical case to be normally unstable (Section V). Evaporation is, in fact, found to proceed in statically grossly unstable configurations under a dynamic balance depending drastically on viscous shear. The "Haines Jumps" in the foreground of earlier accounts [1 - 3] can occur only in much larger passages than would appear realistic for soils, oil recovery or fabrics. Instead, the normal state in evaporation is one of slow liquid motion leaving the small menisci almost stationary, while most of the mass-evaporation occurs at the large ones (Section VI). These results furnish a basis (Section VII) for statistical estimates of macroscopic evaporation rates, provided enough is known about the statistical distribution of capillary throat sizes. Such knowledge appears to be an absolute prerequisite for any useful treatment of fluid motion in porous media because viscous shear depends so violently on throat size. As a result, if two media have the same chemistry and identical shape for their respective void passages, but differ in mere geometrical scale, then microscopic dynamic balances can be quite different. This discourages constitutive theories of porous media, of which invariance to geometric scale is a basic premise.

There are other caveats, for instance, if the vapor-air mixture must pass through small throats, the significant gasdynamical processes must be anticipated to change the evaporation rate drastically. On the other hand, there are also many bits of luck, which make a realistic fluid mechancis of porous media more accessible. In particular, the extreme magnitudes of relevant combinations of physical parameters will come to explain, by and by, why errors by only a factor 2, or so, will be treated so cavalierly.

II. STATIC EQUILIBRIUM. When the escape of the air-vapor mixture is unobstructed, the pressure throughout that gas is effectively the ambient pressure, P_a. Admittedly, since surface tension promotes evaporation, thermal equilibrium between liquid and vapour requires a gas pressure at their interface which depends on the meniscus curvature. Helmholtz' analysis [4], however, shows this to be a threshhold effect, and for realistic capillary bores, the thermal conditions here envisaged are well below the threshhold [5]. With the apparent contact angle β measured as in Figure 1, the pressure on the liquid side of a meniscus is therefore

$$P_\ell = P_a - 2\sigma/a, \qquad (1)$$

where a denotes the local capillary radius and $\sigma \sec \beta$, the surface tension. It will be assumed that $0 < \beta < \pi/2$, for otherwise, surface tension would have kept the liquid out of the porous matrix. Body forces will be neglected. Since it is prohibitive to take account of all the shapes of void-passage cross-sections liable to occur in a porous matrix, a will be defined by

πa^2 = area of cross-section; the error in (1) is then one of those treated cavalierly.

By (1), a connected liquid column is in static equilibrium if, and only if, a takes the same value at all the menisci bounding the column. The equilibrium is stable if, and only if, a does not decrease with distance along the capillary measured toward the gas side at any of those menisci (Fig 2).

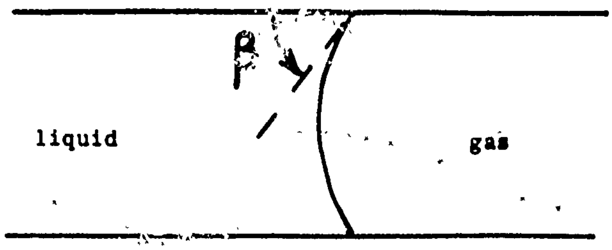

Figure 1

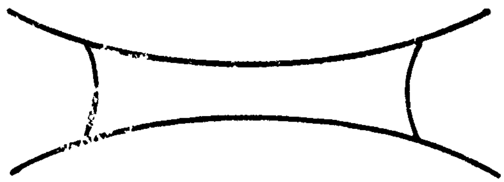

Figure 2a. Stable equilibrium

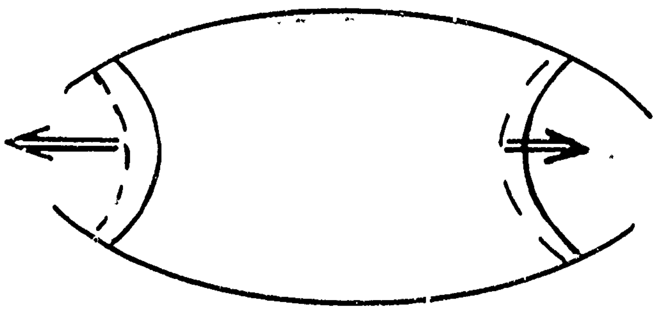

Figure 2b. Unstable equilibrium

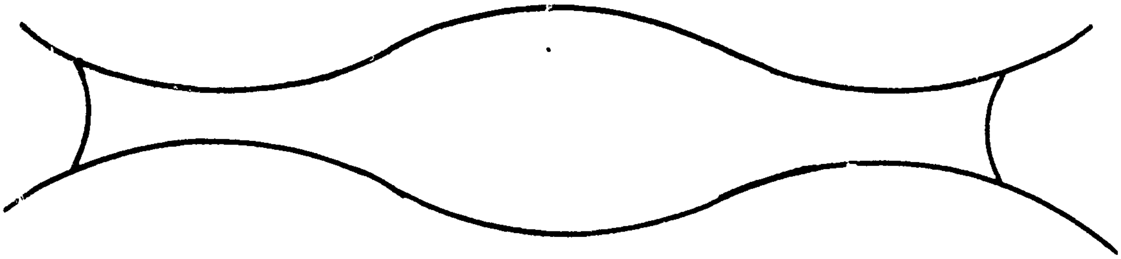

Figure 3

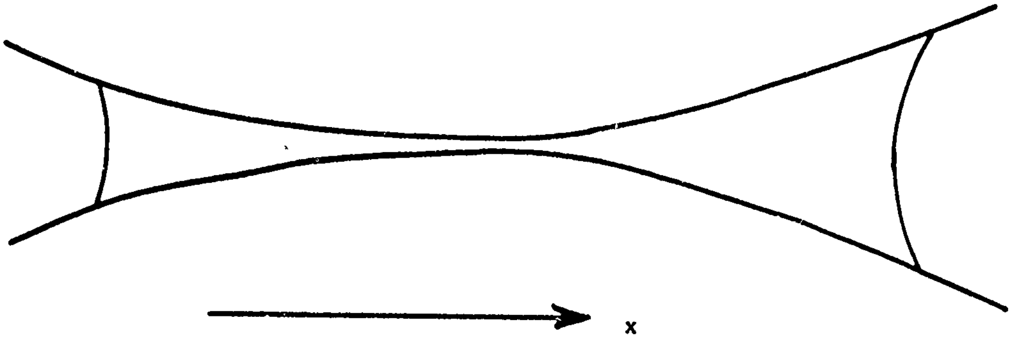

Figure 4

Those are merely local conditions, however. All kinds of void-passage shapes can be expected in a porous matrix. Figure 3 indicates one with a liquid column in a position of stable equilibrium. Suppose, however, that this liquid volume be reduced by, say, 30%, e.g., by evaporation. The remaining liquid column could not then find a stable equilibrium position anywhere in the passage segment shown : it must move to find a new, stable position elsewhere. The need for such "Haines jumps" [1] in the liquid configurations has dominated the literature on the physics of fluids in porous media [1 - 3] : on kinematic considerations, they would be expected to be sudden and frequent so that fluid motion could appear as a continuous process only on a long-term average [3]. Analysis of the dynamics (Section VI), however, will show that such notions can be relevant only to unrealistically large passages.

III. THERMAL BALANCE. Prolonged evaporation must depend on an external heat supply, and it might be anticipated that, not only the rate, but also the manner, of that supply has a major influence on the evaporation process. However, since the ratio of capillary volume to surface area is proportional to the capillary bore, heat transfer across the capillary wall is always important in small capillaries. That transfer will be found in section IV to cause an adjustment of temperatures in the fluid and solid that reduces the influence of the manner of heat supply. To fix the ideas, it will be envisaged that a reservoir supplies it to the solid matrix, in the first place, so as to heat it gradually, from the original, uniform temperature T_0 of the whole medium, which may be considered to be known, to a level T_1 at which it is then maintained. Specifically, T_0 may be the outdoor temperature, and T_1 may be near body-temperature, perhaps $T_1 \approx T_0 + 50°F$. The properties of the solid are outside the scope of this study and will be assumed uniform. This does not imply a temperature field constant in time and uniform in space, because evaporation makes the menisci act like moving heat sinks of changing strength, but the space-average T_w of the capillary wall temperature will change only slowly with time. The stronger, local variation in capillary wall temperature can be accounted for approximately by rough adjustments [5] and meanwhile, the considerations can be simplified by ignoring the difference between T_w and the local temperature of the capillary wall. That will lead to estimates of evaporation at menisci in terms of T_w, whence estimates of the time development of T_w by more global considerations will follow.

Since little can be known about the shapes of realistic void-passage cross-sections, the description of evaporation will be simplified greatly by representing quantities in the fluid by their averages over a capillary cross-section and ignoring the errors resulting from use of somewhat different averages in different contexts. The thermal description is also greatly simplified, if no liquid motion couples the processes at different menisci. That is possible in the idealized case of a capillary of radius $a(x)$ even in distance x along the capillary, if the temperature field is similarly even and liquid fills a capillary segment between menisci at $x = \pm \ell$, with $a'(\ell) > 0$ for static stability (Fig 2a). Such symmetry can

persist, at least in principle, and will be assumed in this Section and the next one.

The local thermal balance per unit length is then

$$\pi a^2 \rho_\ell c_\ell \frac{\partial T_\ell}{\partial t} = \frac{\partial}{\partial x}\left(\pi a^2 \lambda \frac{\partial T_\ell}{\partial x}\right) + 2\pi a h\,(T_w - T_\ell),$$

where the lefthand side represents the local rate of increase of liquid heat content; ρ and c denote density and heat capacity, respectively, and the suffix ℓ distinguishes liquid properties. The first term on the righthand side represents the contribution from heat conduction in the liquid, and the last term, that from heat transfer across the capillary wall on the most rudimentary, conventional model of a heat transfer rate per unit wall area and unit temperature difference represented by a constant transfer coefficient h. With the insignificant further approximation of neglect of variations in λ, ρ_ℓ and c_ℓ, the balance becomes

$$\frac{\partial T_\ell}{\partial t} = \frac{\kappa}{a^2}\frac{\partial}{\partial x}\left(a^2 \frac{\partial T}{\partial x}\right) + \frac{2h}{\rho_\ell c_\ell a}(T_w - T_\ell) \tag{2}$$

where κ denotes the usual heat diffusivity, $\kappa = \lambda/(\rho_\ell c_\ell)$. The liquid therefore experiences a typical heat conduction process with variable effective diffusivity, on account of the capillary shape, and with heat transfer, but without convection, on account of the symmetry.

A somewhat different balance arises at a meniscus. Since the liquid and gas are there envisaged in dew-point equilibrium to begin with, and since the gas pressure remains at the ambient level p_a until Section VIII, any heat reaching the meniscus will result meanwhile in evaporation, but not [2] in a change of the local temperature T_M from its original level T_0. Conduction through the liquid column in $x < \ell$ contributes heat to the meniscus at the rate

$$-\pi a_m^2 \lambda (\partial T_\ell/\partial x)_{x=\ell} \quad ,$$

if the meniscus is at $x = \ell(t)$ and a_m denotes the capillary radius $a(\ell)$ there. Conduction through the gas in $x > \ell$ does not contribute comparably because its heat conductivity is smaller. If the meniscus is markedly curved, heat reaches it also by direct transfer across a short segment of the capillary wall and radial heat conduction. The wall area from the meniscus contact line to the position of its apex (Fig 1) is approximately $2\pi a_m^2 \alpha_2$ with $0 < \alpha_2 = \sec\beta - \tan\beta < 1$. The rate of heat transfer across

this area is

$$2\pi a_m^2 \alpha_2 h_M (T_w - T_M) ,$$

where h_M denotes a value of the transfer coefficient h adjusted [5] to compensate for the error made by confusing the local wall temperature at the meniscus with its level further away.

Let S denote a short capillary segment of fixed length which is stationary in a frame moving with the local, liquid velocity and which contains the meniscus at present. The gas pressure and temperature are constant in S, and if $D\ell/Dt$ denotes the velocity of the meniscus in that frame, the mass-rate of evaporation in S is

$$m = -\pi a_m^2 \rho_\ell D\ell/Dt . \tag{3}$$

The mass of gas in S does not increase at a significant rate because the density ratio ρ_g/ρ_ℓ is about 10^{-3}, in the circumstances envisaged, so that vapour leaves S at the same mass-rate, and the net rate of mass loss in S is also m, since no liquid enters S. By the First Law, the net rate of liquid enthalpy loss in S equals the rate of vapor enthalpy loss from it less the rate of heat addition by transfer and conduction into S,

$$\pi a_m^2 [2\alpha_2 h_M (T_w - T_M) - \lambda \partial T_\ell/\partial x] = mL, \tag{4}$$

where L is the latent heat per unit mass.

IV. THERMAL LAYER. The use of these balances requires a nondimensional notation, and it is not obvious whether a single length scale X can be representative of the temperature field throughout a liquid column. Even without attention to cross-sectional shape, the capillary is described by the two functions a(x) and a'(x)/a(x) of normally quite different magnitued and each of which may vary by orders of magnitude along a capillary. To avoid confusion, let attention be confined first to a liquid column segment adjacent to the initial meniscus position $x = \ell(0)$ and short enough to occupy only a capillary segment characterized by a single triplet of scales a_0 of the capillary radius, G, of a(x)/a'(x) and X, of the unknown temperature variation. But, there is another thermal length scale,

$$\Lambda = (\tfrac{1}{2}\lambda a_0/h)^{\frac{1}{2}} ,$$

of decisive significance because Λ^2/X^2 represents the ratio of the thermal diffusion scale to the transfer scale. How is X related to the other three length scales?

The present model can give no information on how Λ compares with a_0 and G, but a more detailed calculation [5] shows that Λ must be anticipated to be of the order of the capillary radius, so that

$$\Lambda/a_0 = [\lambda/(2a_0 h)]^{\frac{1}{2}} = \gamma_h$$

is a parameter of order unity; a rough estimate [5] is $\gamma_h \approx \frac{1}{2}$. Accordingly, $X = a_0$, unless this be found to imply that $T_\ell(x)$ can vary only on a longer

scale. The natural temperature-difference scale is $T_w - T_M = \Delta$, and if

$$T_w - T_\ell(x,t) = T(x,t)\,\Delta \quad ,$$

t is measured in units of a time scale τ, a/a' in units of G, and x, a and ℓ, in units of $X = a_0$, then the nondimensional form of (2) and (4) is

$$\frac{a_0^2}{\kappa\tau}\frac{\partial T}{\partial t} - \frac{2a'}{a}\frac{a_0}{G}\frac{\partial T}{\partial x} = \frac{\partial^2 T}{\partial x^2} - \frac{1}{\gamma_h^2 a}\, T \tag{5}$$

and

$$\frac{\partial T}{\partial x} + \frac{\alpha_3}{\gamma_h^2} = -\frac{a_0^2}{\epsilon\kappa\tau}\frac{d\ell}{dt} \quad \text{at } x = \ell(t),$$

respectively, because

$$T(\ell,t) = 1$$

in this notation and because the liquid is at rest; here $\alpha_3 = \alpha_2 h_M/h$ and

$$\epsilon = c_\ell \Delta/L \ll 1$$

in the circumstances here envisaged, eg, $\epsilon = 1/20$ for water and $\Delta = 50°F$.

Two different time scales have emerged from the balances. The shorter, a_0^2/κ, characterizes transients arising from imbalance of heat transfer and conduction which might be anticipated, eg, in a Haines jump. It is normally a rather small fraction of a second, eg, if $\kappa = 10^{-3}cm^2/sec$ and $a_0 = 10^{-2}cm$, then $a_0^2/\kappa = 10^{-1}sec$. The motion of the meniscus, on the other hand, is on the longer time scale

$$a_0^2/(\kappa\epsilon) \; .$$

The first question must be whether a relatively stable evaporation process is possible, and to examine this, the time scale τ must be identified with $a_0^2/(\kappa\epsilon)$. If also $a_0/G \ll 1$, as one would usually expect, then the lefthand side of (5) becomes unimportant by comparison to the righthand terms, in which $a^{-1} \approx 1$, to the same approximation. The balances then imply

$$T = \exp\frac{x-\ell(t)}{\gamma_h} \; , \qquad \ell(t) = \ell(0) - \frac{\gamma_h+\alpha_3}{\gamma_h^2}\, t \tag{6}$$

[except when the capillary segment under scrutiny contains $x = 0$, in which

case

$$T = 2^{-\ell(t)/\gamma_h} \quad \cosh(x/\gamma_h)].$$

This solution describes a very short meniscus layer, of thickness equal to the thermal length scale $\Lambda = \gamma_h a_0$, in which virtually the whole process of heat transfer to, and heat conduction in, the liquid takes place.

This conclusion destroys the analysis sketched so far because one of its main premises -- that thermal balances can be formulated in terms of cross-sectional averages -- cannot apply to precisely the short capillary segment containing the curved meniscus and all significant temperature gradients! Any tenable analysis of the temperature field must account for the geometry of the meniscus, but that depends mainly on matters accessible only to vague speculation, at best, namely the shape of the capillary cross-section and the apparent contact angle.

If a tenable analysis could be performed, on the other hand, it would necessarily lead to the same dimensional groups and would therefore also predict a dimensional meniscus velocity of the form

$$\gamma \frac{\kappa\varepsilon}{a_0} = \gamma \frac{\lambda(T_w - T_M)}{a_0 \rho_\ell L}$$

and a dimensional evaporation time of the form

$$\gamma^{-1} \ell_0 a_0 / (\kappa\varepsilon)$$

for a capillary segment of length a_0. What has no rational support is the value $(\gamma_h + \alpha_3)/\gamma_h^2$ of the nondimensional coefficient γ predicted by (6).

Thought about extreme cases indicates however, that the correct value of γ cannot plausibly be far from order unity and indeed, that $\gamma = 3$, 4 or 5 cannot usually be very wrong. To fix the ideas, therefore, the value $\gamma = 4$ will be adopted speculatively for illustration. For water (with $\kappa \approx 0.0014$ cm^2/sec) and $\varepsilon = 1/20$, various capillary radii and lengths then give roughly the meniscus velocites and evaporation times listed in the following table.

TABLE 1

	a_0(cm)					
	10^{-2}	10^{-3}		10^{-4}		
$4\varepsilon\kappa/a_0$	3×10^{-2}	3×10^{-1}		3		cm/sec
ℓ_0	10^{-1}	10^{-1}	10^{-2}	10^{-2}	10^{-3}	cm
$\ell_0 a_0/(4\varepsilon\kappa)$	3	$\frac{1}{3}$	$\frac{1}{30}$	3×10^{-3}	3×10^{-4}	sec

In sum, the analysis has been wrong in everything but its result. Most of all, what has been proven, if only by contradiction, is that the temperature variation associated directly with evaporation from a meniscus must be quite local. It follows that the main results are also independent of some other premises There can be no significant, direct thermal interaction between different menisci even if the liquid moves on the time scale $a_0^2/(\kappa\epsilon)$; the meniscus velocity should then be interpreted as that of the meniscus relative to the adjacent liquid and a_0 must represent the scale of the capillary radius a_m at the instantaneous meniscus position. The manner of heat supply, moreover, can have less direct influence on the local process than might have been thought at first : apart from the local dip in solid temperature at the meniscus (accounted for by a correct value of γ) the solid temperature background of a capillary must reflect the macroscopic scale of the solid matrix as a whole and must therefore appear effectively uniform on the length scale a_0 of the local evaporation process.

In the first place, (6) applies only to a capillary segment in which the radius differs by less than an order of magnitude from that at the initial meniscus position. Once evaporation has cleared that segment, however, an analogous calculation with a different scale a_0 applies to the next segment. Since narrow segments are seen to clear in a much shorter time than wide ones, it does not appear worth entering here upon the refinement of replacing a_0 from the start by the capillary radius $a_m(t)$ at the meniscus.

V. INSTABILITY. Before evaporation, all menisci bounding a connected liquid column must be of the same size (Section II), but in a realistic porous medium $a'(x)$ cannot also be expected to have the same value at different such menisci. The meniscus velocity (Section IV) then takes the same value at all the initial menisci positions, but if they all started to move with it, static equilibrium would be lost promptly. Surface tension acts towards restoring it, but the differences in meniscus velocity relative to the liquid act in the opposite sense. Stability of evaporation therefore poses a question different from that of static stability (Section II).

To examine it, consider a liquid column bounded by two menisci at which the gas pressure, p_a, and temperature, $T_M = T_0$, remain the same, but at which the capillary radii differ. To illuminate the distinction from static stability, suppose $a'(x)$ is monotone over the whole liquid-filled capillary segment, which contains a throat (Fig 4). Denote the meniscus positions by $x = \ell_+$ and $x = \ell_- < \ell_+$ and the capillary radii there, by $a(\ell_+) = a_+$ and $a(\ell_-) = a_- < a_+$, respectively; ie, the smaller meniscus is at the lefthand end of the liquid column. By (1), surface tension generates a pressure difference

$$p(\ell_+) - p(\ell_-) = 2\sigma \frac{a_+ - a_-}{a_+ a_-}$$

driving the liquid towards the left.

If $a'(x)$ is not too large, the viscous shear generated by the ensuing liquid motion sets up a pressure gradient related approximately by Poiseuille's formula

$$Q = -\frac{\pi\rho}{8\mu} a^4 \frac{dp}{dx}$$

to the mass-flow rate Q (counted towards the right), which is independent of x, by mass conservation. Since liquid density variation is insignificant,

$$p(\ell_+) - p(\ell_-) = -\frac{8\mu Q}{\pi\rho} \int_{\ell_-}^{\ell_+} [a(x)]^{-4}\, dx,$$

and since the main contribution to this integral arises from the throat region, it promotes clarity to write the integral as ℓ_t/a_t^4 in terms of the throat radius a_t and a "throat length" ℓ_t. The mass-flow rate generated by surface tension is then

$$Q = -\frac{\tau\rho\sigma}{4\mu} \frac{a_t^4}{a_+ a_-} \frac{a_+ - a_-}{\ell_t}$$

and the corresponding cross-sectional averages of liquid velocity are $Q/(\pi\rho a_+^2)$ at the right meniscus and $Q/(\pi\rho a_-^2)$, at the left one.

Evaporation, on the other hand, retracts the menisci into the liquid with velocities $\gamma\kappa\epsilon/a_+$ and $\gamma\kappa\epsilon/a_-$, respectively (Section IV). The center of the liquid column therefore shifts at the rate

$$\frac{d}{dt} \frac{\ell_+ + \ell_-}{2} = \frac{\kappa\epsilon}{2} \frac{a_+ - a_-}{a_+ a_-} \left[\gamma - \left(\frac{a_t^2}{a_+ a_-}\right)^2 \frac{a_+^2 + a_-^2}{4Ce\, a_0 \ell_t} \right] ,$$

where

$$Ce = \epsilon\kappa\mu/(\sigma a_0)$$

is a capillary number based on evaporation velocity and is normally very small, if the apparent contact angle is not close to 90° (Fig 1); for water, eg, $4a_0 Ce \sim 10^{-8}$ cm. The factor of Ce^{-1} in the last bracket, however, tends to be even smaller, as long as a_+ and a_- remain large

compared to the throat radius a_t. During such a phase of evaporation, the liquid column therefore shifts towards the right, ie, in the direction opposite to that suggested by surface tension alone. Any statically stable liquid configuration with $a_m >> a_t$ is therefore unstable under evaporation.

If the menisci were found close to the throat, on the other hand, in the last stage of evaporation, then the second term in the last bracket would be large, the liquid column would move leftward, and the smaller meniscus would move away from the throat.

In sum, most of the evaporation must be anticipated to occur in liquid configurations that are not static equilibria, and there might be preferred positions for the smallest menisci.

VI. DYNAMIC BALANCE. For a realistic impression of evaporation in porous media, one must therefore consider liquid configurations far from static equilibrium, for instance, such as indicated in Figure 5, which envisages a situation that might be seen in a snapshot of a "Haines Jump" after evaporation has made one meniscus clear a throat. The disparity of the meniscus sizes then generates a marked pressure difference driving the liquid towards the smaller meniscus, and an unsteady liquid motion must be anticipated. There are two very small time scales, namely the liquid column length divided by the sound speed in it and the time scale a_t^2/ν of viscous diffusion of shear from the capillary wall in the throat region (Fig 5), which is about 10^{-4}sec in water, if $a_t \sim 10^{-3}$cm. The evaporation time scales (Section IV) are much longer, and the full viscous shear must therefore be expected to have been established, particularly in the throat region. The drastic degree to which this viscous shear in small capillary throats will be seen presently to control evaporation illustrates the reason for the prominence of Darcy's law in porous fluid mechanics.

The pressure imbalance drives a mass-flow rate $Q(t) < 0$, since it is directed towards the smaller meniscus (Fig 5). At the same time, the menisci retract into the liquid with their respective evaporation velocities $\gamma\kappa\varepsilon/a_+$ and $\gamma\kappa\varepsilon/a_-$ (Section IV). It will promote clarity, and help to distinguish the more generic case from that discussed in the preceding Section, to exploit the disparity in meniscus sizes (Fig 5) to the degree of neglecting a_- against a_+. The larger meniscus is then considered to move just with the velocity $dx_+/dt = Q/(\pi\rho a_+^2)$, but the smaller, to move with the velocity

$$dx_-/dt = \gamma\kappa\varepsilon/a_- + Q/(\pi\rho a_-^2) \qquad (7)$$

relative to a fixed frame. The pressure difference is now approximated as $p_+ - p_- = 2\sigma/a_-$ and the total shear stress is $-8\mu\, Q\ell_t/(\pi\rho a_t^4)$, in

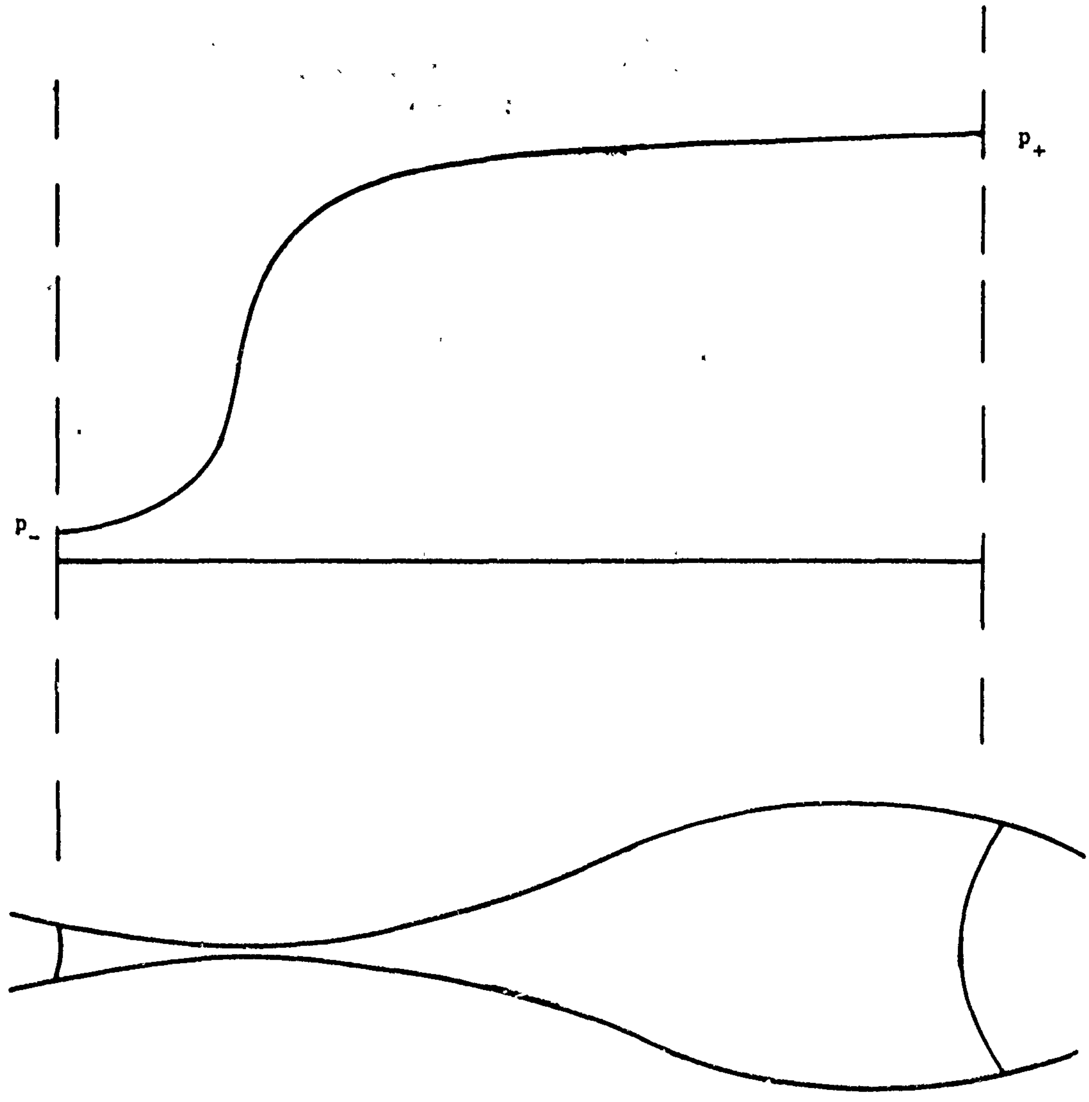

Figure 5

terms of the "throat length" ℓ_t of Section V. In small capillaries, the pressure drop and viscous shear cannot come into significant imbalance, and therefore,

$$2\sigma/a_- = -8\mu\, Q\ell_t/(\pi\rho a_t^4).$$

This is the microscopic version of Darcy's law for liquid motion driven through a small capillary by surface tension $\sigma\sec\beta$ at menisci of disparate size. Since it relates Q to a_-, (7) may be written

$$a_- \frac{dx_-}{dt} = \gamma\epsilon\left[1 - \frac{\sigma}{4\gamma\epsilon\kappa\mu\ell_t}\left(\frac{a_t^2}{a_-}\right)^2\right] ,$$

and since $da/dx < 0$ at the position $x = x_-(t)$ of the smaller meniscus (Fig 5), this shows the approximate dynamics to be represented by an equation of the structure

$$c_1 \frac{d}{dt}(a_-^2) = \frac{c_2}{a_-^2} - 1, \qquad 1/c_1 = -2\gamma\epsilon a'(x_-) > 0, \tag{8}$$

and with increasing time, a_-^2 must approach

$$c_2 = \sigma a_t^4/(4\gamma\epsilon\kappa\mu\ell_t) .$$

This does not represent a strict equilibrium because T_w, and therefore also ϵ, may change slowly with time, and in any case, the liquid keeps moving, but only a minor drift of the smaller meniscus results therefrom. In terms of a hybrid capillary number

$$Ct = \epsilon\kappa\mu/(\sigma a_t)$$

based partly on evaporation and partly, on throat radius, the smaller meniscus remains close to the position where

$$a_-/a_t \sim (4\gamma Ct\ell_t/a_t)^{-\frac{1}{2}} . \tag{9}$$

The capillary radius at the smaller meniscus is thus seen to depend most of all on the throat radius, indeed, to be proportional to a_t^2, on account of the dominance of viscous shear in small capillary throats. For a rough impression, for water, $\epsilon = 1/20$, $a_t = 10^{-3}$cm and sec $\beta = 2$, the hybrid capillary number is $Ct \sim 10^{-5}$; a value 15 of 4γ is unlikely to be wrong by a large factor, and if $\ell_t = 20a_t$, then the last formula

predicts $a_-/a_t \sim 20$. Figure 5, accordingly, gives a reasonable impression of a typical configuration. Table I gives an impression of the liquid velocity : for $a_t = 10^{-3}$cm, eg, it is only about 10^{-2}cm/sec at the smaller meniscus, and the velocity dx_+/dt of the larger meniscus relative to a fixed frame is even less.

Most of the mass-evaporation, on the other hand, occurs at the larger meniscus (Fig 5) because its area is larger; by (3), it is

$$m = \pi\gamma\rho\kappa\varepsilon a_+ = \pi\gamma a_+ \lambda(T_W - T_M)/L \quad . \tag{10}$$

For water and $a_+ = 1$mm, eg, it would be about 10^{-7}gr/sec. In turn, an impression of the dependence of the wall-temperature level T_W upon the external heat supply begins to emerge, because the rate Q_h of that supply per meniscus is mL. In a liquid column bounded by just two menisci of disparate size, the smaller expends relatively little of this, so that (10) shows the external heat supply to such a column to depend only on T_W and on the capillary bore at the larger meniscus.

The critical importance of capillary size merits re-emphasis here. The pressure difference due to surface tension is proportional to a_m^{-1}, and so is the meniscus velocity relative to the liquid, but the pressure drop due to viscous shear is proportional to a_t^{-4}. Accordingly, if two porous samples be compared which are identical in regard to chemistry and to shape of the void-passages, but differ by a factor 10 in the size of those passages, then the dynamic balances for them differ by, essentially, a factor 10^3 and therefore, the fluid physics in the two samples may be quite different. That contrasts strongly with constitutive theories of porous-media mechanics, of which invariance under mere change of geometric scale is a main premise. It appears doubtful, therefore, that a substantive description of fluid mechanics in porous media is obtainable without some insight into the fluid dynamics on the microscopic level, whence macroscopic behavior must spring.

VII. MACROSCOPIC IMPLICATIONS. For an impression of global evaporation in a porous medium, a thermodynamically steady phase may need to be distinguished from an initial, transient phase. The later phase is characterized by essential equality, at any time, of the rates of external heat supply and of latent-heat expenditure. The global mass-rate of evaporation is then immediately known and a lower bound τ_0 of total evaporation time can be deduced as that which evaporation of the initial liquid mass would need under such conditions.

Whether such a late phase occurs at all, or at the other extreme, whether the transient phase is of no importance, must be judged from comparison of τ_0 with the time scale of the transient phase. The latter may be one of three scales, of which the first, τ_1, characterizes the rate at which the external reservoir can communicate heat to the porous aggregate and a second, τ_2, characterizes the rate at which heat can be distributed through the solid matrix. Neither of these is within the scope of this account, but the time scale τ_3 of liquid response to the heat supplied to it can be predicted on the basis of the present results, if adequate knowledge of the statistical distribution of void-passage sizes is at hand.

Indeed, if even a relatively small number of large passages thread the porous aggregate, then all the "action" will occur in them, and Haines Jumps may be there observable, while the rest of the medium remains essentially inert until the by-passes have cleared to an extent making them effectively a part of the outer boundary of the medium.

On the other hand, if enough passage throats of sufficiently small size are distributed sufficiently well through the aggregate, then they will anchor the liquid and permit only creeping motion. The time scale τ_3 would then be expected to be essentially that of transition from static stability to dynamic balance, which (8) shows to be

$$\tau_3 = c_1 a_0^2/(\kappa\epsilon) = (a_0/\epsilon)^2/[2\gamma\kappa|a'(x_-)|].$$

Since it is seen to depend most of all on a_0 and ϵ, a useful, macroscopic estimate of this scale requires both a judicious choice of ϵ between 0 and its level in the steady stage, and also a statistically valid measure πa_t^2 of the cross-sectional areas of small throats, whence the corresponding measure a_0 of capillary radii at the small menisci can be deduced by (9). For a very rough impression (which may well be misleading in regard to specific cases), if $\epsilon = 1/50$, $a_0 = 10^{-2}$ cm and $|a'(x_-)| = 10$ were appropriate, then for water, $\tau_3 \sim 4$ min.

If τ_3 should turn out to be much longer than τ_0, τ_1 and τ_2, the microscopic dynamics of the main phase of evaporation would be that described in Section V. The stability analysis there given is not linearized, and its results therefore apply to the whole transition from static stability to dynamic balance. Of course, once the initial configuration of static stability has been left well behind, the much simpler approximation of Section VI becomes adequate. The translation here of the microscopic description into a predictive algorithm on the macroscopic scale

may be premature, however, because its usefulness is likely to depend critically on a more precise knowledge of the statistical distribution of void-passage sizes than appears available to-date for any real sample.

VIII. VAPOR TRANSPORT. For evaporation in dynamic balance, the time-dependence of the processes in the air-vapor mixture may also be expected to amount to no more than a slow drift leaving the processes quasi-steady. Transfer from the capillary wall will heat this gas, but if the pressure differences in it are insignificant because no small throats obstruct its passage, then the attendant density change will not be worth accounting for, at the temperature levels here envisaged.

Accordingly, the volume flow rate $\pi a^2 u$ of gas will also be considered constant along the passage.

The mass evaporated consists of vapor, but the gas flow moves the air-vapor mixture and must therefore be accompanied by diffusion of vapor and air into each other. The gas at the meniscus must be at its dew point, so that the partial vapor pressure there is the saturation pressure at the meniscus temperature T_M. For water vapor, e.g., that partial pressure is about 1/40 (or 3/40) at $T_M \approx 293$ (or 313)° K, and the gas even at the meniscus then consists almost entirely of air. Since the partial vapor density is even smaller [4], the diffusion of the vapor is adequately approximated by the standard, linear model of Fick's law, $j_v = -\theta\nabla\rho_v$, for the vapor flux. With unsteadiness already neglected, the same mass-flow rate of vapor must cross every capillary cross-section, so that $\pi a^2 u\rho_v - \pi a^2 \theta d\rho_v/dx$ is independent of x. It follows that

$$\frac{\rho_v - \rho_{vm}}{\rho_{ve} - \rho_{vm}} = e^{(\xi-\xi_e)/q},$$

where subscripts m and e distinguish respective values at meniscus and capillary exit,

$$\xi = a_m^2 \int_{x_m}^{x} [a(s)]^{-2}\, ds,$$

and $q = \theta/u_m$ is a diffusion-length scale based on the gas velocity u_m at the meniscus. Most of the diffusion therefore occurs within a ξ-distance q of the exit, by contrast to the heat transfer, most of which occurs fairly close to the meniscus.

The process can be radically different, however, if the gas must pass through a small throat. Let u denote again the cross-sectional average of the gas velocity and let subscripts ℓ, g, v, a, m and t distinguish reference to the liquid, gas, vapor, air, meniscus and throat, respectively. Then from the estimate of meniscus velocity relative

to the liquid in Section IV, $a_m u_m = \gamma\varepsilon\mu_\ell\rho_\ell/\rho_v$, approximately, and since this is independent of meniscus size, so is the Reynolds number $Re_m = a_m u_m/\nu_a$ of the gas-flow at the meniscus. Since $\nu_a \approx 0.15\ cm^2/sec$ and $\rho_\ell/\rho_v \approx 10^3$ for water, Table 1 (Section IV) indicates $Re_m = 2$ to be a rather typical value. The mass-flow rate $m = \pi a^2 \rho_g u$ is independent of x in near-steady evaporation, and apart from the influence of density changes, the local Reynolds number $Re = au/\nu_a$ of the gas-flow varies in proportion to $a_m/a(x)$. For most plausible values of a_m/a_t, the gas-flow therefore remains laminar even in a throat, and the pressure drop can again be estimated from Poiseuille's formula,

$$a\ dp/dx = -\ 8\mu_a m/(\pi a^3 \rho_g) = -\ 8\mu_a a_m^2 u_m/a^3,$$

where $8\mu_a a_m u_m$ is independent of meniscus size and typically, $\approx 5 \times 10^{-7}$ gr when $\mu_a = 2 \times 10^{-7}$ gr sec/cm^2.

If now $a_m = 10^{-2}$ cm, to fix the ideas, then $a_m/a_t = 10$ yields a value of 5×10^{-3} atm for $|a\ dp/dx|$ at the throat, and the pressure drop is insignificant. If $a_m/a_t = 100$, however, then the estimate suggests a value of 5 atm for $|a\ dp/dx|$ at the throat, and not only the estimate, but clearly also, most of the premises and assumptions of this Note, collapse. If the evaporation estimates remained valid when the gas must pass through very small throats, they would imply major gasdynamical effects in such throats, the work expended on them would play a major role in the thermodynamic balances, and the meniscus temperature T_M could not be expected to be close to the initial, ambient temperature T_0; the physics of evaporation would be quite different from that here described. Accordingly, the microscopic physics of evaporation may depend rather drastically on whether a porous medium is formed into a sheet-like or ball-like aggregate...

The great sensitivity of quantitative estimates to void-passage size suggests that a profitable discussion of fluid mechanics in porous media may need to relate to quite specific circumstances. In particular, if thought returned to fabrics, it appears unlikely that the same microscopic physics could describe evaporation from wool, gore-tex or pile.

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